An overview of millimeter-wave spectroscopic measurements of chlorine monoxide at Thule, Greenland, February-March, 1992: Vertical profiles, diurnal variation, and longer-term trends

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Abstract. Measurements of chlorine monoxide in the stratosphere over Thule, Greenland (76.3N, 68.4W) were made quasi-continuously during the period February 8 to March 24, 1992, using a high-sensitivity ground based mm-wave spectrometer. These observations give diurnal, short term, and long term changes in the mixing ratio and vertical distribution of ClO. At an equivalent time after the *Antarctic* winter solstice, very large concentrations (up to ~1.5 ppbv) occur in lower stratospheric ClO, resulting in massive ozone destruction. We saw no evidence for large (~1 to 1.5 ppbv) amounts of ClO in the 16-25 km range over Thule in February or March, in agreement with UARS (satellite) observations by the MLS mm-wave spectrometer for this period, and in marked contrast to UARS/MLS and ER-2 aircraft measurements over northern Europe and eastern Canada, respectively, during January, 1992. We have evidence for smaller enhancements (~0.2 to 0.5 ppbv) in the 18-30 km range during late February-early March, which could result from transport of residual low NO_2 air following earlier PSC processing (the last of which occurred at least one month earlier, however) or the result of chemical processing by Pinatubo aerosols. Direct influence of Pinatubo aerosols on Arctic ozone during the spring of 1992 has been difficult to assess, and this enhancement of low-altitude ClO might be a significant indicator of aerosol effects.

Introduction

Since the initial discovery of the Antarctic ozone hole it has been realized that the strength, extreme coldness, and isolation of the southern winter vortex favors heterogeneous chemical processing on a scale and for a duration not likely to occur in the Arctic. The discovery of a general downtrend in northern hemisphere ozone over the past 10-15 years (e.g., Stolarski, et al., 1991) has turned attention to less dramatic levels of Arctic winter-spring vortex chemical processing, yet prior to the winter of 1991-92, the only measurements of ClO had been made via ER-2 flights within the Arctic vortex of 1989,

and all at times earlier than the equivalent photochemical period of major ozone depletion over Antarctica. In early February, 1989, these showed surprisingly large mixing ratios of up to ~1 ppbv around 19 km (nearly as large as found in the Antarctic vortex at comparable altitudes) (Brune, et al., 1991), but were not accompanied or followed by massive ozone loss.

Wide-area mapping of stratospheric ClO during January 1992 by the MLS mm-wave spectrometer onboard NASA's Upper Atmospheric Research Satellite (UARS) showed, near mid-month, a geographically extensive layer at about 20 km altitude, with mixing ratios 1-1.5 ppbv, in the sunlit stratosphere over northern Europe and western Russia (Waters, et al., 1993). Near this region, temperatures were low enough to allow polar stratospheric cloud (PSC) formation (Braathen, et al., 1992). ER-2 aircraft measurements also showed high concentrations of ClO in the 15-18 km range over eastern Canada in January, 1992, when part of the vortex had moved particularly far west (D. Toohey, et al.,to be published in *Science*, 1993). Despite these indications of an Arctic lower stratosphere poised for large scale ozone depletion, very little ozone loss occurred for the remainder of the spring.

The mere observation of ClO in the lower stratosphere does not presage a massive destruction of ozone: concentrations must remain large and temperatures must remain low for a significant length of time. The most rapid catalytic cycle allowing ozone destruction in the lower stratosphere involves ClO dimer formation (Molina and Molina, 1987) via the three-body process $ClO + ClO + M \rightarrow Cl_2O_2 + M$. Here, efficiency increases proportionally to the square of [ClO], as well as linearly from the increase in [M] at lower altitudes, and can cause rapid O_3 destruction at mixing ratios ≥ 1 ppbv in the 15-25 km range (Barrett, et al., 1988).

During February and March, temperatures throughout the Arctic region were typically >205K (Braathen, et al., 1992), well above those associated with either Type I or Type II stratospheric clouds, and there was no further chemical processing by PSCs. The eruption of Mt. Pinatubo in June of 1991, however, produced a major increase in sulfuric acid aerosols that extended throughout the Arctic by the winter of 1991-92 (see other EASOE reports, this issue). Rapid heterogeneous reactions on these aerosols are thought to be efficient for removal of NOx. These reactions operate at temperatures too warm for PSCs (though they will be less efficient in sunlight, due to photolysis of N_2O_5), and aerosol surface reactions may have continued to suppress NOx without additional PSC processing.

We consider here data taken at Thule, Greenland (76.3 N, 68.4 W) during a critical period from February 8 to March 24, corresponding to that when massive ozone loss occurs over wide regions of Antarctica south of ~70°.

Data Analysis

Emission line spectra of the ClO rotational transition at 278.6 GHz were measured using a new, highly sensitive superconducting detector system, with a bandwidth of 512 MHz and resolution of 1 MHz (de Zafra, et al., 1993). Spectra were later smoothed by a 5 MHz weighting function to improve S/N ratios. This does not degrade spectral line shape information below an altitude of ~48 km. (The pressure-broadening coefficient for ClO is ~3.3 MHz/mb for the temperatures relevant here (Pickett, et al., 1981)).

Sunrise-to-sunset time at 16 km altitude increased from ~4.3 hours on February 9 (day 40), to ~14.5 hours on March 20 (day 80). The respective daylight times at 40 km are 6.5 hours and 17 hours. The noon solar zenith angle changed from 92° to 77.5° between February 9 and March 20. (True solar exposure times counting from sunrise each day are somewhat shortened by the proximity of the solar terminator to the northward, and the predominantly north-to-south trajectories of air over Thule at speeds of 50-100 km/h (Braathen, et al., 1992)).

a. Long-term evolution of ClO column density.

For optically thin sources such as ClO, the integrated intensity under a clean spectral line is linearly proportional to the total column density, if the spectral bandwidth is large enough to cover the entire lineshape.

To establish vertical column density trends through February and March, we typically averaged three consecutive days' mid-day emission spectra together to improve the S/N ratio and reduce spectral artifacts. Bad weather accounts for some averages over longer time spans. Errors in derived column densities are estimated to be 15-20% at the 60% confidence limits.

To establish how much of the observed February increase in ClO column density was due to increasing solar flux driving standard chlorine chemistry in the mid-to-upper stratosphere, and how much to growth of an anomalous ClO layer in the lower stratosphere, we have integrated line intensities over three different spectral widths: ±230, 180 and 130 MHz around the line center. Results are plotted in Fig. 1. The general trend in column density is an increase of nearly six-fold during February, then a drop in later March. Growth in mid-day total column density during February is expected from increasing hours of sunlight and the decreasing solar zenith angle, but growth at different altitudes has very different implications. Derived column densities for the two broader integration windows are essentially the same. Values for the narrowest window fall below the others for late February and early March, thus showing that some of the increase in total column density between days ~56 and 75 comes from an increase in lower, more pressure-broadened ClO. The amount and altitude range can be more directly assessed via pressure-broadened line shape deconvolutions to obtain vertical profiles, which we address in the next section.
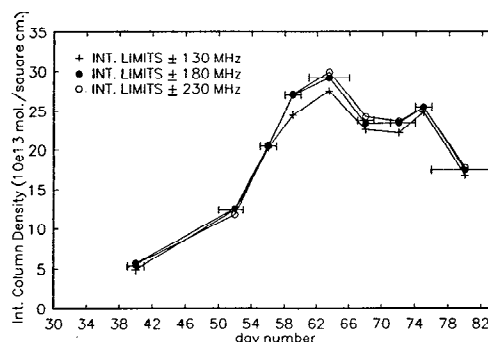

Fig. 1. Vertical column density above 16 km vs. time. Feb. 9 = Day 40, Mar. 24 = Day 84. Horizontal bars indicate time spans covered by points. Column density uncertainties are estimated at ≤20%. Results are given for three integration limits, symmetric about the emission line center.

b. Evolution of Vertical Profiles.

Selected line shapes are contrasted in Fig. 2 with a ClO measurement made with the same instrument at McMurdo Station, Antarctica, a few months later, in September 1992. The February 27-March 6 data were chosen to illustrate the period of greatest low-altitude emission evident in our observations, while the McMurdo data is typical, rather than extreme. Deconvolution of the latter yields a ClO mixing ratio of ~1.5 ppbv in a low altitude layer centered about 18 km. This has been consistent in all years sampled to date, (de Zafra, et al., 1987, 1989, and unpublished data, 1991, 1992), reaching a maximum by mid-to-late September. Note that the March 17-24 Thule data and the September 19-22, 1992 McMurdo data of Fig. 2 fall at equal times after the respective winter solstice, and that each location is about equidistant from the respective pole, so that diurnal exposure to solar flux was very nearly the same for each case. Despite the early and severe depletion of Arctic NOx in the winter of 1991-92, it is evident that the
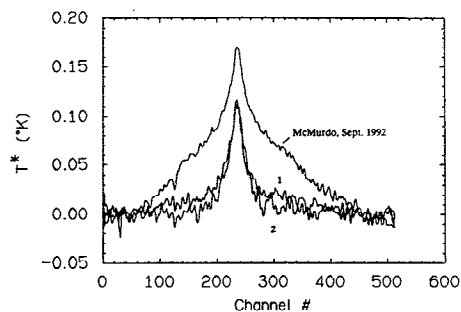

Fig. 2. ClO spectral line shapes at Thule, Greenland, vs. McMurdo Station, Antarctica. Strong line wings in the Antarctic data are generated by pressure-broadened emission from a distinct low altitude layer of ClO. Slight line wings are seen in the Feb. 27-Mar. 6 average, (1), relative to (2), Mar. 17-24, when air from the Aleutian region moved in. The ordinate gives radiation intensity in equivalent Rayleigh-Jeans temperature units. The abscissa is spectrometer channel number, at 1 MHz per channel.

resulting chemical/dynamical history of the lower stratosphere in springtime was markedly different from that over McMurdo. Although our Thule data pertain to air near the periphery of the Arctic vortex of 1991-92, they agree with mid-February to late March UARS/MLS measurements of ClO within the remaining vortex core (Waters, et al., 1993).

We now turn to line shape deconvolutions to obtain vertical profiles, using a modified Chahine-Twomey deconvolution method (Twomey, et al., 1977). Examples recovered from mid-day line shapes are given in Fig. 3. They show an enhanced amount of ClO in the range below 30 km in late February-early March. The role played by dynamics is evident: increase in column density and in low-altitude ClO between mid-February and mid-March coincided with a westward shift of the vortex core, bringing core-processed air (thus lower in NOx content) closer to Thule, while the decrease in later March accompanied a major circulation shift bringing in stratospheric air from the Aleutian high for the first time in 1992. (See Emmons, et al., this issue, for further analysis of this dynamical shift.) The weakness of the line wings makes the recovered lower profiles uncertain, however this data (or subsets of it) always yield profiles varying between the extremes of a non-specific enhancement spread between ~30 to 15 km, and a weak but distinct layer peaking a little below 20 km: *in no case are line shapes consistent with more than a few tenths of a part per billion ClO below 30 km.* Early February and late March data yield no significant low layer.

c. Diurnal Variation.

We have chosen here the period February 27-March 6 to study dirunal variation. This period show the greatest evidence of low altitude ClO enhancement. Also, by this

Table 1. Vertical column densities in units of 10^{13} molecules/cm^2 averaged over 2/27-3/06. Uncertainties are shown in parentheses. Time code is 1 = 2-0 h predawn at 40 km; 1n = successive 2-h averages, starting from dawn; 2n = successive 2-h averages running backwards from sunset; 3n = 2-h averages running forward after sunset.

time	±230 MHz	±180 MHz	±130 MHz	±50 MHz
1	2.3(0.4)	2.9(0.5)	3.4(0.6)	3.7(0.7)
11	7.1(1.3)	7.3(1.3)	6.5(1.2)	4.7(0.8)
12	14.3(2.6)	14.0(2.5)	13.4(2.4)	8.0(1.4)
13	27.8(5.0)	27.3(4.9)	25.0(4.5)	9.4(1.7)
23	30.7(5.5)	29.9(5.4)	27.8(5.0)	10.4(1.9)
22	23.3(4.2)	22.9(4.1)	20.9(3.8)	7.7(1.4)
21	14.1(2.5)	14.6(2.6)	12.5(2.2)	4.4(0.8)
31	2.8(0.5)	2.6(0.5)	2.5(0.4)	3.7(0.7)
32	2.7(0.5)	2.8(0.5)	3.3(0.6)	3.5(0.6)

time, the sun was high enough to lessen the impact of north-south transport. We have averaged spectral data into 2 h time bins chosen with respect to sunrise and sunset at 40 km. (Sunrise and sunset at 15 km differ by at most ~1 h from the times at 40 km during the Feb. 27-March 6 period, and at most ~1/2 hour at 25 km.)

Table 1 shows vertical column densities derived for four integration widths. Values for the first three columns have been computed using the area above a linear baseline intersecting the data curve, averaged over 20 channels, centered at ±230 MHz. Note baseline noise causes some statistically insignificant "trends" in rows 1 and 32, where the signal is weak. The last column is integrated above a linear baseline fitted around the ± 50 MHz intersections. This underestimates the column density near mid-day for this column, but is consistent with the treatment of Mauna Kea data in the comparison discussed below.

The diurnal variation of ClO in the upper stratosphere (primarily right hand column, table 1) is markedly less than seen in 1982 at 19.5°N over Mauna Kea, Hawaii (Solomon, et al., 1984). The Thule data shows no statistically significant change over a ±50 MHz integration from the first two hours after sunset to the final two hours before dawn, whereas the Mauna Kea data showed a ratio of $3.1^{+2.3}_{-1.2}$. The time between sunset and sunrise at 35 km was about the same for each data set, averaging ~12.3 h at Thule and ~11.9 h at Mauna Kea, so this is not responsible for the difference. The prolonged low solar elevation angles at Thule should shift the $ClO/ClONO_2/HOCl$ equilibrium in favor of the latter two reservoir species however, and significant reversion to the reservoirs may occur before sunset. If, instead, the mid-day to pre-dawn ratio is compared, we find $2.8^{+1.0}_{-0.7}$ for Thule vs $5.5^{+4.1}_{-2.0}$ for Mauna Kea, i.e., somewhat better agreement, but still indicating a significant difference in the gas-phase photochemistry at high latitudes.

We also note that a current AER model (J. Rodriguez, private communication) yields a much greater rate of morning rise and predawn/midday ratio of column densities for this time period and latitude than we have observed here.
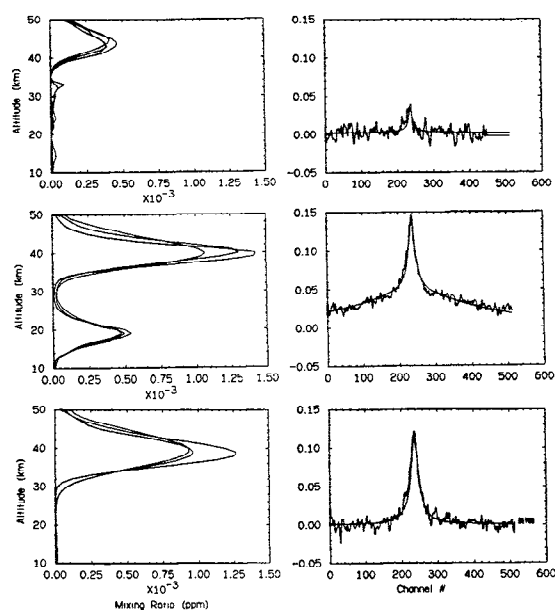

Fig. 3. Left panels: vertical profiles recovered from observed emission line shapes. Illustrated range of profiles all give good fits within noise in data. Right panels: Observed line shapes vs shapes synthesized from recovered profiles. Top panels, Feb. 8-10; middle panels, Feb. 27-Mar. 6; bottom panels, Mar. 17-24.

Summary

In *early* February we have found relatively little ClO in the stratosphere over northern Greenland, consistent with the limited exposure to sunlight. Within our limits of detection, this appeared to be located only in the upper stratosphere, where the "standard" chlorine cycle forms ClO as soon as there is enough solar radiation to release Cl from its nighttime reservoirs. In late February and early March, there is evidence for enhancement of ClO at low altitudes, but this was not very intense, and could no longer be detected when air from the Aleutian high moved over Thule in later March. Observations at Thule covered a period of similar solar exposure at very nearly the same polar latitude as various measurements we have made during September 1986, 1987, 1991 and 1992 at McMurdo Station, Antarctica. The latter have invariably shown a durable and extensive layer of ClO, with a peak mixing ratio approaching 1.5 ppbv at ~18-20 km altitude by late September, directly involved with a period of rapid and massive ozone destruction. Our 1992 Thule data show no persuasive evidence for more than a few tenths ppbv of ClO between ~16-30 km throughout the equivalent period. This enhancement may result from transport of air 'denoxified' by earlier PSC processing near the vortex center, from sulfuric aerosol processing, or some combination of both. Diurnal variation studies indicate significant differences may be present relative to to that observed at 20°N, and to predictions of some current models for high-latitude gas phase chemistry.

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